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Hydrated sulphuric acid in dense molecular clouds

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ABSTRACT

We consider sulphur depletion in dense molecular clouds, and suggest hydrated sulphuric acid, $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$, as a component of interstellar dust in icy mantles. We discuss the formation of hydrated sulphuric acid in collapsing clouds and its instability in heated regions in terms of the existing hot core models and observations. We also show that some features of the infrared spectrum of hydrated sulphuric acid have correspondence in the observed spectra of young stellar objects.

Key words: ISM: clouds – dust, extinction – ISM: lines and bands – ISM: molecules – infrared: ISM.

1 INTRODUCTION

Observations of sulphur-bearing and other molecular species in dense molecular clouds have established that elemental sulphur is more depleted by two orders of magnitude than are carbon, oxygen and nitrogen (Joseph et al. 1986; Kemper et al. 1999). Current chemical models of translucent clouds imply that sulphur is depleted by factors exceeding 10 with respect to its average abundance in diffuse clouds, where all the elemental sulphur appears to reside essentially in the gas phase (Snow & Witt 1996).

The supposed large depletion of sulphur relative to the other elements may be illusory as a consequence of the existence of an unobservable form of molecular sulphur, S_2 , which could be the major carrier of the elemental sulphur. S_2 has been suggested to be ubiquitous in comets (A'Hearn et al. 2000), where it could be produced in the innermost coma via fast reactions between OCS and atomic sulphur in the metastable ^1D state. In interstellar clouds, the sulphur dimer might attain large abundances in hot cores (Charnley 1997), but its concentration is unlikely to be significant in cold regions (Ruffle et al. 1999).

A possible hypothesis is that the missing sulphur is locked up in icy grain mantles. In star-forming regions, only trace amounts of solid-state sulphur are detected (Palumbo, Geballe & Tielens 1997). Gas-phase chemistry of sulphuretted molecules implies that S, SO and CS are important reservoirs of sulphur in the gas. Oxidation of these species on grain surfaces will lead to SO_2 and OCS, which have both been identified in the grain mantles. The subsequent hydrogenation would lead to the formation of H_2S , H_2CS and CH_3SH (Palumbo et al. 1997). None of these species is present on the icy

surfaces of interstellar grains (Gibb et al. 2000). However, the discovery of iron sulphide, FeS, in two Herbig stars (Keller et al. 2002) points to a chemistry where the bulk of the sulphur depletion is accomplished by incorporation into dust grains.

There is no strong infrared band that can be assigned to sulphur compounds in icy mantles. Hence the solid-state sulphur must be in a form which has infrared modes that are (presently) inaccessible, or obscured by much broader spectral features. In this paper, we discuss the depletion of sulphur from the gas phase in the formation on grains of a weakly refractory material, the hydrated sulphuric acid $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$.

2 THE FORMATION OF SULPHURIC ACID ON GRAINS

Sulphuric acid aerosols are ubiquitous in our atmosphere and they have been observed also in the atmosphere of Venus (Krasnopolsky 1994). The production of H_2SO_4 is widespread in the terrestrial atmosphere, where it takes place naturally as a consequence of volcanic injection of materials, and anthropogenically from combustion of fuels. Oxidized sulphur forms readily in hydrocarbon combustion where sulphur is a minor impurity in the fuel (Brown et al. 1996a,b). The detailed kinetics of atmospheric sulphuric acid aerosols is uncertain. It appears essential that a surface be available and there is some indication that the chemical composition of the refractory cores is inconsequential (Brown et al. 1996c). There is little evidence for a strong chemical interaction between carbon particles and H_2SO_4 , and it is likely that particulates such as $(\text{SiOH})_4$, Fe_2O_3 and MgCO_3 provide a condensed phase for reaction. Therefore in an oxidizing environment there appears to be a ubiquitous chemistry through which sulphur is oxidized to sulphuric acid.

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That much of the sulphur is in the form of S^+ ions in translucent clumps led Ruffle et al. (1999) to suggest an enhanced depletion rate of sulphur during the clump collapse. Ions collide more rapidly with grains and may stick more efficiently to them than do neutral species. Eventually in the collapse, gas-phase sulphur becomes incorporated in neutral species, still allowing for sulphur-bearing species in dense cores to be detectable. The reaction chain to form sulphuric acid on grain surfaces probably begins with the neutralization of S^+ ions which thermalize to the grain temperature T_d and are adsorbed on the surface (Shalabiea & Greenberg 1994), followed by reaction with OH to produce SO. Subsequent reactions with OH end with the formation of sulphuric acid:



The production rate of H_2SO_4 can be estimated as

$$\frac{dn_4}{dt} = \eta_1 \eta_2 \eta_3 k_0 n_S n_{OH}, \quad (1)$$

where n_4 , n_S and n_{OH} are the surface abundances of H_2SO_4 , sulphur and OH, respectively, k_0 is the second-order rate coefficient of the triggering reaction between S and OH, and $\eta_{1(2,3)}$ is the efficiency of reaction $R_{1(2,3)}$ as the exit channel of $SO(SO_2, HSO_3)$:

$$\eta_j = \left(1 + \frac{D_j}{k_j n_{OH}}\right)^{-1} \quad (j = 1, 2, 3). \quad (2)$$

In equation (2), D_j (s^{-1}) and k_j ($cm^3 s^{-1}$) are the total destruction rate of the sulphur-bearing reactant and the rate coefficient of reaction R_j , respectively. We describe the rate coefficients of surface reactions as

$$k_j = \kappa_j \frac{(\tau_{hop,r1}^{-1} + \tau_{hop,r2}^{-1})}{N_s n_d} \quad (3)$$

(Hasegawa, Herbst & Leung 1992; Herbst 1995), where κ_j is an efficiency factor, $\tau_{hop,ri}$ (s) is the time-scale of thermal hopping of the i th adsorbed species, N_s is the number of surface sites, and n_d is the grain number density. The hopping rate is given approximately by the expression

$$\tau_{hop,ri}^{-1} = \nu_0 \exp(-E_b/T_d), \quad (4)$$

where ν_0 is the vibrational frequency of the adsorbate and E_b (K) is the potential barrier between two sites of potential minima. Quantum mechanical tunnelling rates are negligible for species heavier than H atoms.

With hopping potential barriers of 330 and 378 K for S and OH, respectively (Hasegawa et al. 1992), we get $\tau_{hop,S}^{-1} = 4.7 \times 10^{-2} s^{-1}$ and $\tau_{hop,OH}^{-1} = 3.8 \times 10^{-4} s^{-1}$. Then the H_2SO_4 formation rate in equation (1) becomes

$$\frac{df_4}{dt} = \mathcal{R} \sim 1.12 \times 10^{18} \eta^3 f_S f_{OH} \text{ Myr}^{-1}, \quad (5)$$

where f_4 , f_S and f_{OH} are the fractional surface abundances of H_2SO_4 , S and OH, respectively. Following Hasegawa et al. (1992), in equation (5) we set $\kappa \sim 1$ for atoms and radicals involved in the reaction. We adopt $n_d = 1.33 \times 10^{-12} n_H$, where n_H is the concentration of H nuclei in all forms, and $N_s = 10^6$. We approximate the product $\eta_1 \eta_2 \eta_3$ by the cube of an average factor η . Setting $f_S \sim 1 \times 10^{-5}$, roughly the cosmic abundance of sulphur (Snow & Witt

1996), and $f_{OH} \sim 5 \times 10^{-5}$ (Hasegawa et al. 1992), we obtain the formation time

$$\tau_f \sim \mathcal{R}^{-1} = 1.8 \times 10^{-9} \eta^{-3} \text{ Myr}. \quad (6)$$

This time is less than 1 Myr as long as $\eta \gtrsim 0.001$. The derived lower limits on the reaction efficiencies are plausible since there is no evidence of a significant concentration of sulphur-bearing molecules in interstellar ices (Palumbo et al. 1997; Gibb et al. 2000) or in the gas phase in cold dense clouds.

From heat of vaporization and vapour pressure measurements, the vapour pressure of H_2SO_4 can be estimated. Extrapolation of the equilibrium vapour pressure from higher pressures to 10^{-20} atm leads to an equilibrium temperature of 160 K. The vapour pressure of H_2SO_4 is much lower than that of H_2O (Zhang et al. 1993). Thus, clearly not as refractory as standard minerals, sulphuric acid should not be classified as a volatile species.

Once H_2SO_4 is formed it acts to remove H_2O selectively from the vapour phase. There is a considerable body of evidence showing unit accommodation for H_2O on H_2SO_4 (Govoni & Nathanson 1994). Recent measurements by the space-based observatories *ISO* and *SWAS* are placing stringent abundance constraints on CO_2 , H_2O and O_2 . Gaseous water is found to have high abundances in star-forming regions which are consistent with ice mantle evaporation or hydrogenation of atomic oxygen in shocked gas (Gensheimer, Maursberger & Wilson 1996; van Dishoeck & Helmich 1996; Harwit et al. 1998). In contrast, although water ice is ubiquitous along lines of sight towards dense molecular clouds, *SWAS* observations (Snell et al. 2000) indicate a gas abundance significantly below values expected from current steady-state chemical models. Bergin et al. (2000) developed a model in which the depletion of oxygen on to the surfaces of grains, as a result of the hydrogenation into water ice, perturbs the gas-phase chemistry to the point that the remaining gas-phase oxygen is taken up in carbon monoxide, with a small amount in atomic form and, with a much lower concentration, in O_2 . In this case, H_2SO_4 would be only marginally hydrated.

Gas-grain cycling between clumps and the more diffuse inter-clump medium (Charnley et al. 1988, 2001) might change this conclusion. Recently, Goldsmith et al. (2002) reported the tentative detection of molecular oxygen emission in the ρ Oph A cloud. The linewidth and the velocity are consistent with the redshifted wing emission by species that trace the molecular outflows seen in this region. The O_2/H_2 ratio in this high-velocity gas is approximately 10^{-5} , much larger than the low abundances inferred from *SWAS* observations towards dense molecular clouds. Goldsmith et al. (2002) proposed a scenario that explains the low O_2 abundance in cloud cores along with the much enhanced abundance in the outflow region. The quiescent gas is impacted by a shock driven by an embedded young star (or stars). The critical assumption is the evaporation of water ice, which cycles oxygen back to the gas phase. During the warm phase the fractional abundance of gaseous water vapour increases significantly. At later times ($\gtrsim 10^5$ yr) in the cold post-shock gas, there is a steady build-up of water on grain surfaces as a result of direct freeze-out of H_2O molecules and atomic oxygen hydrogenation to form water ice. In this phase, sulphuric acid might be efficiently hydrated.

3 OBSERVATIONAL DATA

Absorption spectra of interstellar ices from the Short Wavelength Spectrometer (SWS) on *ISO* towards two obscured young stellar objects, NGC 7538: IRS9 (Whittet et al. 1996; Schutte et al. 1996) and RAFGL 7009S (d'Hendecourt et al. 1996), can be interpreted to

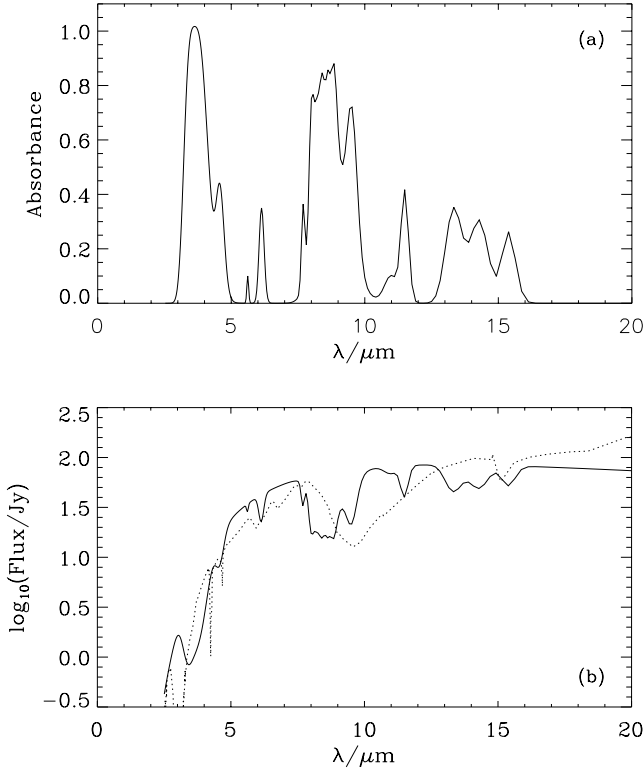


Figure 1. (a) Synthesized laboratory spectrum of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. The absorption coefficient is the sum of 18 Gaussian components. (b) Synthesized spectrum using the absorption coefficient from above. The flux (Jy) is that of a 700-K blackbody reduced by one power in frequency owing to scattering. The dotted line represents a fit to the interstellar spectrum of NGC 7538: IRS9 (Whittet et al. 1996).

provide support for the hypothesis that $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ is an important repository of depleted sulphur. In order to simulate the interstellar spectra, we synthesize the absorption coefficient of mono-hydrated sulphuric acid $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (Zhang et al. 1993) by the sum of 18 Gaussian features shown in Fig. 1(a). In Fig. 1(b) the interstellar spectrum of NGC 7538: IRS9 is superimposed to a synthesized spectrum derived using the absorption coefficient of H_2SO_4 and the

flux of a 700-K blackbody reduced by one power of frequency as a result of scattering.

Table 1 reports the wavelength in μm and wavenumber in cm^{-1} of the major bands of both the interstellar and laboratory spectra.

Of particular interest are the interstellar bands at 6.0 and 9.7 μm which are attributed to H_2O and silicates, respectively. The 6.0- μm feature is too broad to be entirely due to H_2O and contains some extra red and blue absorption (Schutte et al. 1996). The red excess is centred at 6.25 μm and is matched by the 6.19- μm feature in the spectrum of $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$, with the stronger component in mono-hydrated sulphuric acid (Zhang et al. 1993). The broad silicate features seen in both interstellar spectra match and may obscure the absorption exhibited by H_2SO_4 in the 8.0–10.5 μm region. The absorption feature widens and weakens with an increasing number of bound water molecules (Zhang et al. 1993).

The 6.8- μm feature is currently unidentified, but magnesium carbonate MgCO_3 has been proposed (Sandford & Walker 1985; Hect et al. 1986). Magnesium carbonate should have an additional feature near 11.6 μm , which may be the obscured part of the strong extremely broad 9.7- μm band of silicates (Whittet et al. 1996).

The band at 4.67 μm attributed to CO has a corresponding feature in the spectrum of solid $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$, and the 3.0- μm band attributed to solid H_2O is also present in the spectra of crystalline hydrates of sulphuric acid. The centroid of the feature in hydrated sulphuric acid shifts to the red with increasing number of bound water molecules (Zhang et al. 1993).

In the two SWS/ISO spectra four features are present, at 3.0, 4.67, 6.0 and 9.7 μm , that have counterparts in the laboratory spectra of hydrated sulphuric acid, and the intensities of the interstellar bands correlate well with the intensities of the laboratory bands (Zhang et al. 1993). Thus sulphuric acid with incorporated water may be a component of dust together with the other species that are currently assigned. $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ may account for an important part of the depleted sulphur.

4 HOT CORES

Hot molecular cores are believed to represent the earliest steps of massive stellar birth (Walmsley 1992). Hot cores are composed of hot (~ 100 – 300 K), dense ($\sim 10^7 \text{ cm}^{-3}$) gas and warm dust. Chemically, hot cores are characterized by high abundances of fully

Table 1. SWS/ISO peak absorption data in μm (cm^{-1}) for molecular ices towards NGC 7538: IRS9 (Whittet et al. 1996; Schutte et al. 1996) and toward RAFGL 7009S (d’Hendecourt et al. 1996) together with the assignment of the authors and corresponding features in the infrared spectra of crystalline $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ (Zhang et al. 1993).

NGC 7538: IRS9	RAFGL 7009S	Assignment ^a	$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}^b$
15.3	15.2 (657.9) 13.0 (769.2)	CO_2 H_2O	
9.7	9.7 (1030.9)	Silicates	8.0 (1250.0) – 10.5 (952.4)
7.67	7.7 (1298.9)	CH_4	
6.8	6.85 (1459.8)	$\text{MgCO}_3?$	
6.0	6.0 (1666.7)	H_2O	6.19 (1615.5)
4.67	4.67 (2141.3)	CO	4.42 (2262.4) – 4.76 (2100.8)
4.27	4.27 (2341.9)	CO_2	
3.5		CH_3OH	
3.0	3.0 ^c (3333.3)	H_2O	2.56 (3906.2) – 4.0 (2500.0)

^aWhittet et al. (1996); Schutte et al. (1996); d’Hendecourt et al. (1996).

^bZhang et al. (1993).

^cThis band is totally saturated.

hydrogenated molecules such as water, ammonia and hydrogen sulphide, along with a rich variety of complex organics. Such a chemical richness is explained by removal of molecular ice mantles from dust grains owing to evaporation above ~ 90 K, followed by rapid gas-phase ion–molecule reactions. The interaction of the outflows with the envelope produces shocks that can also remove molecular ice from mantles, and drive a high-temperature gas chemistry, involving both ion–molecule and neutral–neutral reactions (Charnley 1997). Hot cores are probably present even in low-mass protostars (Schöier et al. 2002).

Minh et al. (1990) detected large abundances of H_2S towards OMC-1 and also in several other star-forming regions. Large abundances of hydrogen sulphide were also observed in the Orion Plateau source (Minh et al. 1991), where shock chemistry is believed to be important. Ion–molecule gas-phase formation of H_2S is inefficient in hot cores. Although alternative scenarios have been proposed (Minh et al. 1990), the presence of a saturated molecule in a hot core, at an abundance 10^2 – 10^4 times its cold-cloud value, is very strong evidence for a grain surface origin. Erosion of molecular sulphuretted ices could deposit H_2S directly in the gas as a result of the fragmentation and hydrogenation of $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$. In fact, sulphuric acid has not been detected in the gas phase (Hollis et al. 1981), and its hydrogenation to H_2S is thermodynamically allowed. Other species that are likely to be produced from hydrated sulphuric acid by destruction in hot regions are OH, H_2O , SO and SO_2 .

In standard hot-core chemical schemes (Charnley 1997) the abundances of sulphur-bearing molecules like SO, SO_2 , OCS and H_2CS are predicted to be drastically enhanced by the injection of H_2S into the hot-core region. Typically, these species are assumed to be second-generation products. Their abundances ratios can be used to determine the time elapsed since the evaporation of ice mantles has begun (Charnley 1997).

Based on observations of the deeply embedded young stellar object IRAS 16293 – 2422, Schöier et al. (2002) have discussed the possibility of very different chemical time-scales between low-mass and high-mass hot cores. During the formation of a low-mass star, the transit time for grains and molecules through the warm and dense region surrounding the protostar might be extremely fast (\sim a few hundred years). In this case, there would be no enough time for an extensive secondary chemistry to develop (cf. Charnley 1997). Thus the presence of SO and SO_2 with abundances comparable to that of H_2S in IRAS 16293 – 2422 (Schöier et al. 2002) might trace the chemical complexity derived from previous stages of grain mantles and gas-phase chemistry. If $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ is actually a component of interstellar ices, its release from grain surfaces could explain the high $\text{SO}/\text{SO}_2/\text{H}_2\text{S}$ ratios derived towards the young hot core IRAS 16293 – 2422 by Schöier et al. (2002).

5 CONCLUSIONS

The coincidence of features seen in SWS/*ISO* spectra with laboratory infrared spectra supports the suggestion that H_2SO_4 is formed on grains in collapsing clumps and may remove water from the gas phase by further hydrate formation to $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$. Sulphuric acid might be the repository of all the depleted elemental sulphur in dense molecular clouds. Assuming a cosmic O/S ratio of approximately 50 (Snow & Witt 1996), mono-hydrated sulphuric acid would also represent ~ 10 per cent of the depleted oxygen. Products of thermal release of hydrated sulphuric acid might be present in the spectra of very young low-mass hot cores, with abundance ratios significantly different from those observed in higher mass, more evolved objects. Cosmic abundance considerations based on the inventory

of the chemical content of the protostellar environment IRAS 16293 – 2422 (Schöier et al. 2002) show that a fraction of sulphuric acid might be released intact from grain surfaces. Chemical destruction processes act on time-scales much longer than the supposed lifetime of the region. If the early-time chemical scenario for the hot core surrounding IRAS 16293 – 2422 were confirmed, very young low-mass hot cores would provide a suitable environment in which H_2OS_4 emission might be detected.

Recently, Keller et al. (2002) discovered iron sulphide emission from discs surrounding two young stars. Our suggestion of the production of hydrated sulphuric acid during the collapsing phase may provide a link with the diffuse interstellar medium, where sulphur is usually not strongly depleted (Snow & Witt 1996), and evolved young star environments, where FeS has been detected. Retting & Brittain (2002) report the detection of the ro-vibrational bands of CO from the circumstellar material around a number of pre-main-sequence stars, including AB Aurigae, one of the two Herbig stars in which FeS emission has been detected (Keller et al. 2002). CO emission shows evidence that warm gas exists in the inner 50 au of the disc. Thus the formation of FeS may occur subsequently to the hot-core phase and may proceed by channelling products from thermally released H_2SO_4 .

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